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(54) **Electroluminescent iridium compounds with fluorinated phenylpyridines, phenylpyrimidines, and phenylquinolines and devices made with such compounds**

Elektrolumineszente Iridiumverbindungen mit fluorierten Phenylpyridinen, Phenylpyridinen und Phenylchinolinen und solche Verbindungen enthaltende Vorrichtungen

Composés d'iridium électroluminescents contenant des phénylpyridines fluorées, des phénylpyrimidines et des phénylquinolines et dispositifs fabriqués avec ces composés

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| <ul style="list-style-type: none"> <li>• BALDO M A ET AL: "VERY HIGH-EFFICIENCY GREEN ORGANIC LIGHT-EMITTING DEVICES BASED ON ELECTROPHOSPHORESCENCE" APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 75, no. 1, 5 July 1999 (1999-07-05), pages 4-6, XP000850655 ISSN: 0003-6951</li> <li>• BALDO M A ET AL: "High-efficiency fluorescent organic light-emitting devices using a phosphorescent sensitizer" NATURE, MACMILLAN JOURNALS LTD. LONDON, GB, vol. 403, no. 6771, 17 February 2000 (2000-02-17), pages 750-753, XP002183466 ISSN: 0028-0836</li> <li>• DATABASE CAPLUS [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; WANG, YUE ET AL: "(Hydroxyphenyl)pyridine derivative, its metal complexes and application a electroluminescence material" XP002201289 retrieved from STN Database accession no. 133: 315395 &amp; CN 1 245 822 A (JILIN UNIV., PEOP. REP. CHINA) 1 March 2000 (2000-03-01)</li> </ul> | <ul style="list-style-type: none"> <li>• DEDEIAN ET AL: "A NEW SYNTHETIC ROUTE TO THE PREPARATION OF A SERIES OF STRONG PHOTOREDUCING AGENTS: FAC TRIS-ORTHO-METALATED COMPLEXES OF IRIIDIUM (III) WITH SUBSTITUTED 2-PHENYLPYRIDINES" INORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY, EASTON, US, vol. 30, no. 30, 1991, pages 1685-1687, XP001070331 ISSN: 0020-1669</li> </ul> |
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**Description**BACKGROUND OF THE INVENTIONField of the Invention

**[0001]** This invention relates to electroluminescent complexes of iridium(III) with fluorinated phenylpyridines and phenylquinolines. It also relates to electronic devices in which the active layer includes an electroluminescent Ir(III) complex.

Description of the Related Art

**[0002]** Organic electronic devices that emit light, such as light-emitting diodes that make up displays, are present in many different kinds of electronic equipment. In all such devices, an organic active layer is sandwiched between two electrical contact layers. At least one of the electrical contact layers is light-transmitting so that light can pass through the electrical contact layer. The organic active layer emits light through the light-transmitting electrical contact layer upon application of electricity across the electrical contact layers.

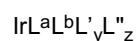
**[0003]** It is well known to use organic electroluminescent compounds as the active component in light-emitting diodes. Simple organic molecules such as anthracene, thiazazole derivatives, and coumarin derivatives are known to show electroluminescence. Semiconductive conjugated polymers have also been used as electroluminescent components, as has been disclosed in, for example, Friend et al., U.S. Patent 5,247,190, Heeger et al., U.S. Patent 5,408,109, and Nakano et al., Published European Patent Application 443 861. Complexes of 8-hydroxyquinolate with trivalent metal ions, particularly aluminum, have been extensively used as electroluminescent components, as has been disclosed in, for example, Tang et al., U.S. Patent 5,552,678.

**[0004]** Burrows and Thompson have reported that fac-tris(2-phenylpyridine) iridium can be used as the active component in organic light-emitting devices. (App/. Phys. Lett. 1999, 75, 4.) The performance is maximized when the iridium compound is present in a host conductive material. Thompson has further reported devices in which the active layer is poly(N-vinyl carbazole) doped with fac-tris[2-(4',5'-difluorophenyl)pyridine-C<sup>2</sup>,N]iridium(III). (Polymer Preprints 2000, 41 (1), 770.)

**[0005]** However, there is a continuing need for electroluminescent compounds having improved efficiency.

SUMMARY OF THE INVENTION

**[0006]** The present invention is directed to an organic electronic device comprising an emitting layer comprising at least one iridium compound having a formula:



where:

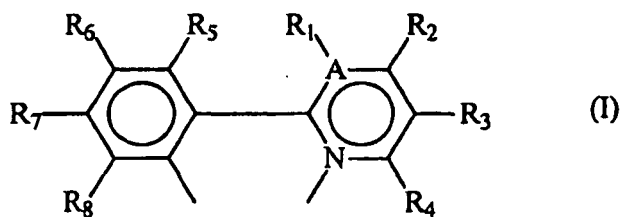
y = 0, 1 or 2, and z = 0 or 1, with the proviso that:

when y = 2 then z = 0;

L' = a bidentate ligand or a monodentate ligand, and is not a phenylpyridine, phenylpyrimidine, or phenylquinoline; with the proviso that:

when L' is a monodentate ligand, y+z = 2, and  
when L' is a bidentate ligand, z = 0;

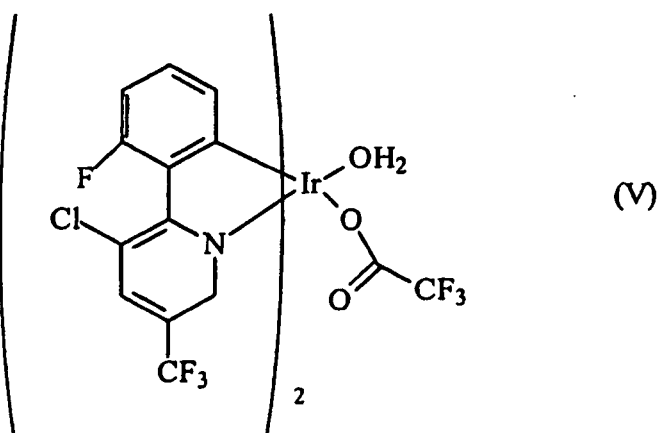
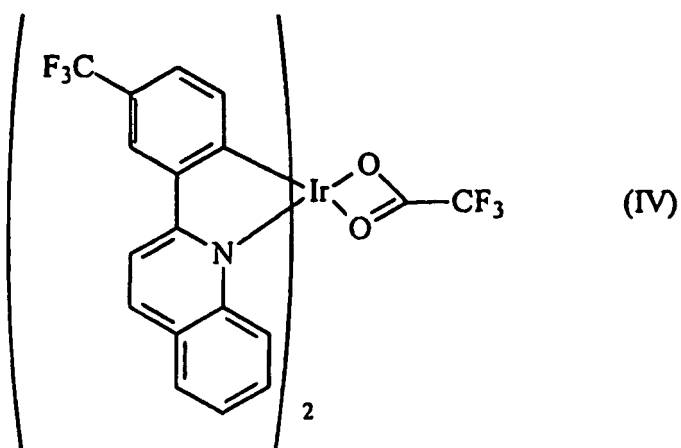
L'' = a monodentate ligand, and is not a phenylpyridine, and phenylpyrimidine, or phenylquinoline; and  
L<sup>a</sup> and L<sup>b</sup> are alike or different from each other and each of L<sup>a</sup> and L<sup>b</sup> has structure (I) below:

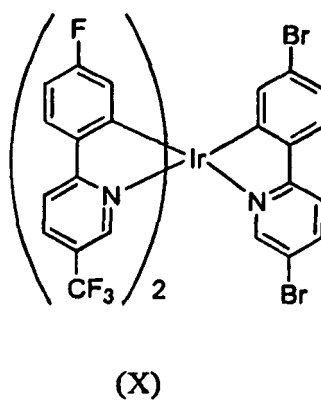
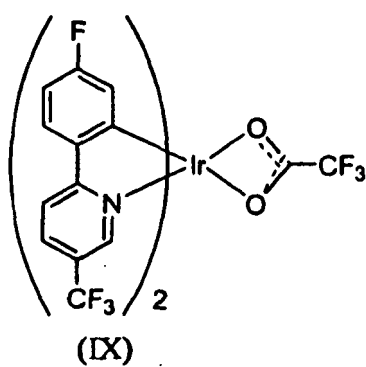
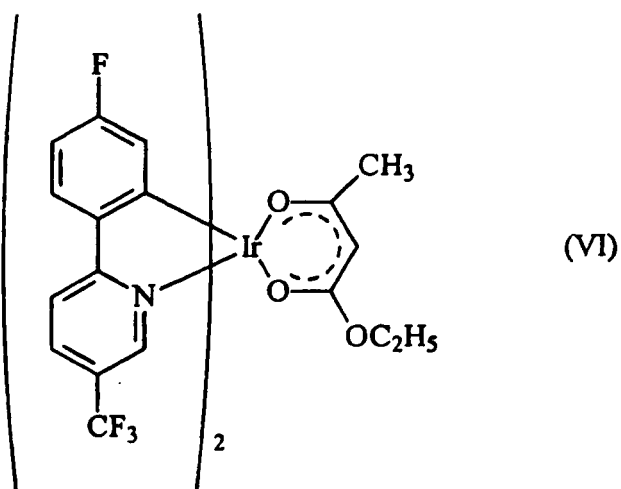


wherein:

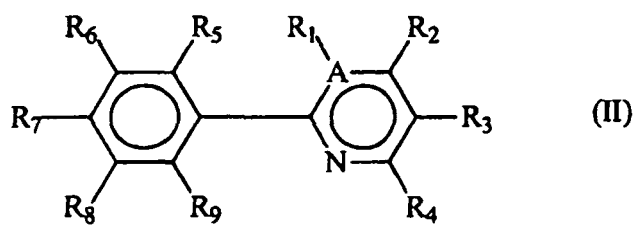
adjacent pairs of  $R_1$ - $R_4$  and  $R_5$ - $R_8$  can be joined to form a five- or six-membered ring, at least one of  $R_1$ - $R_8$  is selected from F,  $C_nF_{2n+1}$ ,  $OC_nF_{2n+1}$ , and  $OCF_2X$ , where  $n = 1-6$  and  $X = H, Cl, \text{ or } Br$ , and  $A = C \text{ or } N$ , provided that when  $A = N$ , there is no  $R_1$ , and with the proviso that when the iridium compound is present in an amount of less than 20% by weight of the emitting layer, the emitting layer comprises a diluent.

**[0007]** In another embodiment, the present invention is directed to a compound having a structure selected from structures (IV), (V), (VI), (IX) and (X) below:

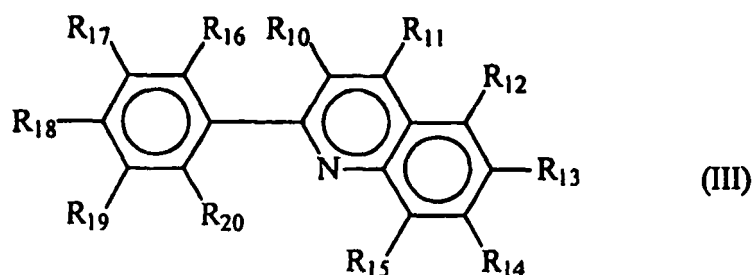




[0008] The above Ir(III) compounds may be made from substituted 2-phenylpyridine, phenylpyrimidine, and phenylquinoline precursor compounds having a structure (II) or (III) below:



where A and R<sub>1</sub>-R<sub>8</sub> are as defined in structure (I) above, and R<sub>9</sub> is H.



where:

at least one of R<sub>10</sub>-R<sub>19</sub> is selected from F, C<sub>n</sub>F<sub>2n+1</sub>, OC<sub>n</sub>F<sub>2n+1</sub>, and OCF<sub>2</sub>X, where n = 1-6 and X = H, Cl, or Br, and R<sub>20</sub> is H.

**[0009]** It is understood that there is free rotation about the phenyl-pyridine, phenyl-pyrimidine and the phenyl-quinoline bonds. However, for the discussion herein, the compounds will be described in terms of one orientation.

**[0010]** As used herein, the term "compound" is intended to mean an electrically uncharged substance made up of molecules that further consist of atoms, wherein the atoms cannot be separated by physical means. The term "ligand" is intended to mean a molecule, ion, or atom that is attached to the coordination sphere of a metallic ion. The term "complex", when used as a noun, is intended to mean a compound having at least one metallic ion and at least one ligand. The term "group" is intended to mean a part of a compound, such a substituent in an organic compound or a ligand in a complex. The term "facial" is intended to mean one isomer of a complex, Ma<sub>3</sub>b<sub>3</sub>, having octahedral geometry, in which the three "a" groups are all adjacent, i.e. at the corners of one face of the octahedron. The term "meridional" is intended to mean one isomer of a complex, Ma<sub>3</sub>b<sub>3</sub>, having octahedral geometry, in which the three "a" groups occupy three positions such that two are trans to each other. The phrase "adjacent to," when used to refer to layers in a device, does not necessarily mean that one layer is immediately next to another layer. On the other hand, the phrase "adjacent R groups," is used to refer to R groups that are next to each other in a chemical formula (i.e., R groups that are on atoms joined by a bond). The term "photoactive" refers to any material that exhibits electroluminescence and/or photosensitivity.

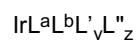
#### DESCRIPTION OF THE DRAWINGS

##### [0011]

Figure 1 is a schematic diagram of a light-emitting device (LED).  
Figure 2 is a schematic diagram of an LED testing apparatus.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0012]** The Ir(III) compounds of the invention have the Formula



where:

y, z, L<sup>a</sup>, L<sup>b</sup>, L', and L'' are as defined above.

Ir(III) compounds having the above Formula are frequently referred to as bis-cyclometalated complexes.

**[0013]** The preferred cyclometalated complexes are neutral and non-ionic, and can be sublimed intact. Thin films of these materials obtained via vacuum deposition exhibit good to excellent electroluminescent properties. Introduction of fluorine substituents into the ligands on the iridium atom increases both the stability and volatility of the complexes. As a result, vacuum deposition can be carried out at lower temperatures and decomposition of the complexes can be avoided. Introduction of fluorine substituents into the ligands can often reduce the non-radiative decay rate and the self-quenching phenomenon in the solid state. These reductions can lead to enhanced luminescence efficiency. Variation of substituents with electron-donating and electron-withdrawing properties allows for fine-tuning of electroluminescent properties of the compound and hence optimization of the brightness and efficiency in an electroluminescent device.

**[0014]** While not wishing to be bound by theory, it is believed that the emission from the iridium compounds is ligand-based, resulting from metal-to-ligand charge transfer. Therefore, compounds that can exhibit electroluminescence include

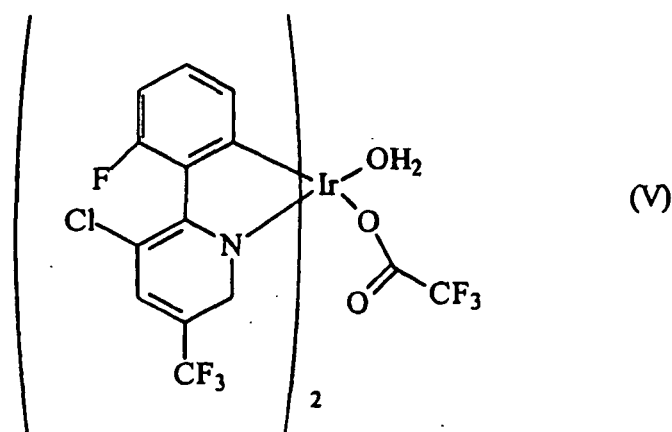
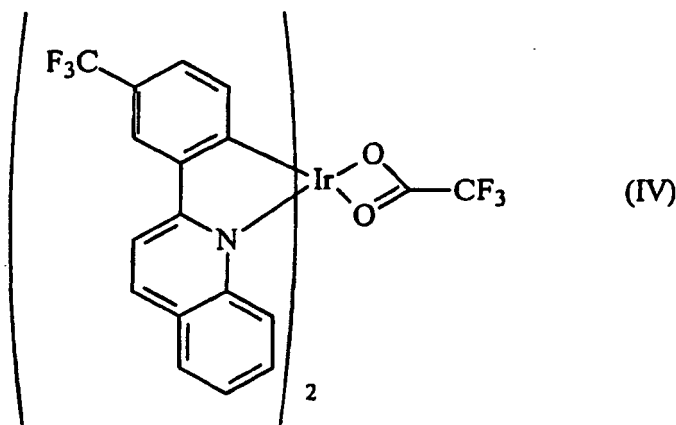
those of compounds of the Second Formula  $\text{IrL}^a\text{L}^b\text{L}'_y\text{L}''_z$  above. The  $\text{R}_1\text{-R}_8$  groups of structures (I) and (II), and the  $\text{R}_{10}\text{-R}_{19}$  groups of structure (III) above may be chosen from conventional substituents for organic compounds, such as alkyl, alkoxy, halogen, nitro, and cyano groups, as well as fluoro, fluorinated alkyl and fluorinated alkoxy groups. The groups can be partially or fully fluorinated (perfluorinated). Preferred iridium compounds have all  $\text{R}_1\text{-R}_8$  and  $\text{R}_{10}\text{-R}_{19}$  substituents selected from fluoro, perfluorinated alkyl ( $\text{C}_n\text{F}_{2n+1}$ ) and perfluorinated alkoxy groups ( $\text{OC}_n\text{F}_{2n+1}$ ), where the perfluorinated alkyl and alkoxy groups have 1-6 carbon atoms, or a group of the formula  $\text{OCF}_2\text{X}$ , where  $\text{X} = \text{H}, \text{Cl}, \text{or Br}$ .

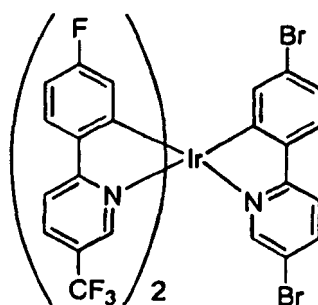
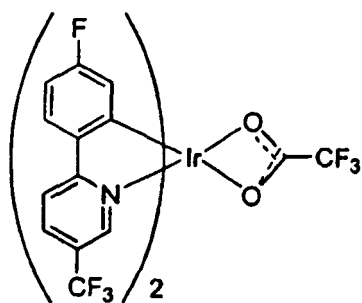
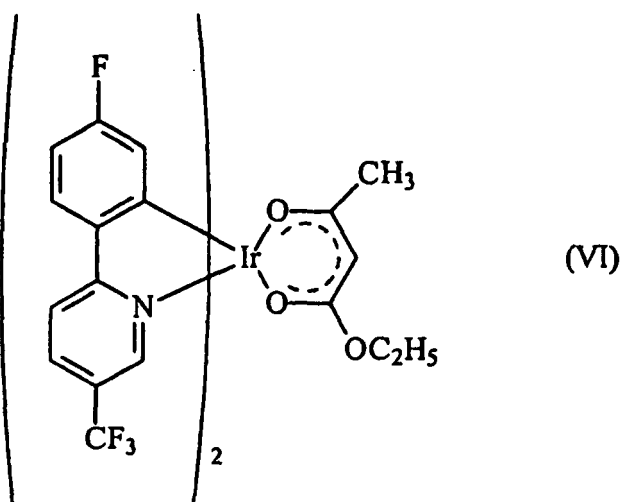
**[0015]** It has been found that the electroluminescent properties of the cyclometalated iridium complexes are poorer when any one or more of the  $\text{R}_1\text{-R}_8$  and  $\text{R}_{10}\text{-R}_{19}$  groups is a nitro group. Therefore, it is preferred that none of the  $\text{R}_1\text{-R}_8$  and  $\text{R}_{10}\text{-R}_{19}$  groups is a nitro group.

**[0016]** The nitrogen-containing ring can be a pyridine ring, a pyrimidine or a quinoline. It is preferred that at least one fluorinated substituent is on the nitrogen-containing ring; most preferably  $\text{CF}_3$ .

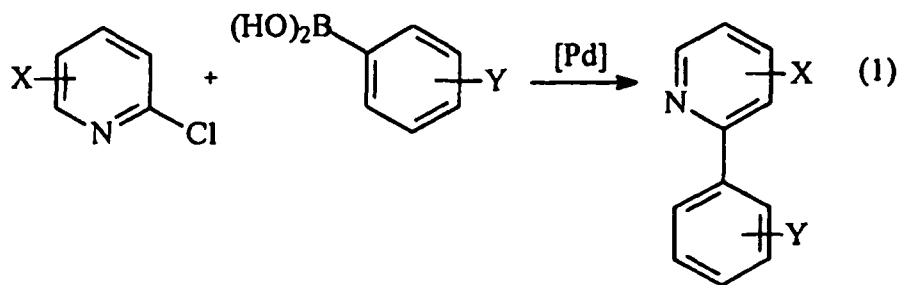
**[0017]** Any conventional ligands known to transition metal coordination chemistry are suitable as the  $\text{L}'$  and  $\text{L}''$  ligands. Examples of bidentate ligands include compounds having two coordinating groups, such as ethylenediamine and acetylacetonate, which may be substituted. Examples of monodentate ligands include chloride and nitrate ions and monoamines. It is preferred that the iridium complex be neutral and sublimable. If a single bidentate ligand is used, it should have a net charge of minus one (-1). If two monodentate ligands are used, they should have a combined net charge of minus one (-1). The bis-cyclometalated complexes can be useful in preparing tris-cyclometalated complexes where the ligands are not all the same.

**[0018]** Example compounds of the Formula  $\text{IrL}^a\text{L}^b\text{L}'_y\text{L}''_z$  above include compounds 1-n, 1-o, 1-p, 1-w and 1-x, respectively having structure (IV), (V), (VI), (IX) and (X) below:





[0019] The substituted 2-phenylpyridines, phenylpyrimidines, and phenylquinolines, as shown in Structure (II) above, are prepared, in good to excellent yield, using the Suzuki coupling of the substituted 2-chloropyridine, 2-chloropyrimidine or 2-chloroquinoline with arylboronic acid as described in O. Lohse, P.Thevenin, E. Waldvogel Synlett, 1999, 45-48. This reaction is illustrated for the pyridine derivative, where X and Y represent substituents, in Equation (1) below:



**[0020]** Examples of 2-phenylpyridine and 2-phenylpyrimidine compounds, having structure (II) above, are given in Table 2 below:

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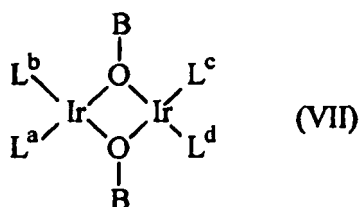
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Compound	A	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	R <sub>5</sub>	R <sub>6</sub>	R <sub>7</sub>	R <sub>8</sub>	R <sub>9</sub>
2-a	C	H	H	CF <sub>3</sub>	H	F	H	H	H	H
2-b	C	H	H	CF <sub>3</sub>	H	H	CF <sub>3</sub>	H	H	H
2-c	C	H	H	NO <sub>2</sub>	H	H	CF <sub>3</sub>	H	H	H
2-d	C	H	H	CF <sub>3</sub>	H	H	F	H	H	H
2-e	C	H	H	CF <sub>3</sub>	H	H	H	CH <sub>3</sub> O	H	H
2-f	C	Cl	H	CF <sub>3</sub>	H	H	H	H	H	H
2-g	C	H	H	H	CH <sub>3</sub>	H	H	F	H	H
2-h	N	--	H	H	H	H	H	F	H	H
2-i	C	H	H	CF <sub>3</sub>	H	H	H	CF <sub>3</sub> O	H	H
2-j	N	--	CF <sub>3</sub>	H	H	F	H	H	H	H
2-k	C	H	H	CF <sub>3</sub>	H	H	H	F	H	H
2-l	C	CF <sub>3</sub>	H	H	H	H	H	H	H	H
2-m	C	Cl	H	CF <sub>3</sub>	H	H	H	F	H	H
2-n	C	CF <sub>3</sub>	H	H	H	H	H	F	H	H
2-o	C	CF <sub>3</sub>	H	H	H	H	H	CH <sub>3</sub> O	H	H
2-p	C	Cl	H	CF <sub>3</sub>	H	H	H	CH <sub>3</sub> O	H	H
2-q	N	--	CF <sub>3</sub>	H	H	H	H	F	H	H
2-r	C	Cl	H	CF <sub>3</sub>	H	H	H	H	H	F
2-s	C	H	H	CF <sub>3</sub>	H	H	H	H	H	H
2-t	C	Cl	H	H	H	F	H	H	H	H
2-v	C	H	H	CF <sub>3</sub>	H	H	CH <sub>3</sub> O	H	H	H
2-w	C	H	CH <sub>3</sub> O	H	H	H	H	CF <sub>3</sub>	H	H
2-x	C	H	H	H	H	H	F	F	H	H
2-y	C	H	H	CF <sub>3</sub>	H	H	F	H	F	H
2-z	C	H	H	CF <sub>3</sub>	H	F	H	F	H	H
2-aa	C	H	H	Br	H	H	H	Br	H	H

**[0021]** One example of a substituted 2-phenylquinoline compound, having structure (III) above, is compound 2-u, which has R<sub>17</sub> = CF<sub>3</sub> and R<sub>10</sub>-R<sub>16</sub> and R<sub>18</sub>-R<sub>20</sub> = H.

**[0022]** The 2-phenylpyridines, pyrimidines, and quinolines thus prepared are used for the synthesis of the cyclometalated iridium complexes. A convenient one-step method has been developed employing commercially available iridium trichloride hydrate and silver trifluoroacetate. The reactions are generally carried out with an excess of 2-phenylpyridine, pyrimidine, or quinoline, without a solvent, in the presence of 3 equivalents of  $\text{AgOCOCF}_3$ . In some cases, mixtures of isomers are obtained. Often the mixture can be used without isolating the individual isomers.

**[0023]** The iridium complexes having the Formula  $\text{IrL}^a\text{L}^b\text{L}^c\text{L}^d$  above can also be prepared by first preparing an intermediate iridium dimer having structure VII below:



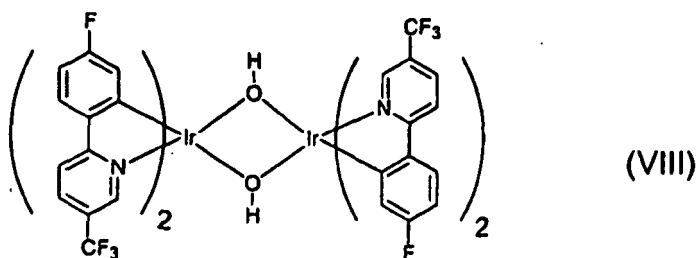
wherein:

$\text{B} = \text{H}, \text{CH}_3, \text{ or } \text{C}_2\text{H}_5,$  and

$\text{L}^a, \text{L}^b, \text{L}^c,$  and  $\text{L}^d$  can be the same or different from each other and each of  $\text{L}^a, \text{L}^b, \text{L}^c,$  and  $\text{L}^d$  has structure (I) above.

The iridium dimers can generally be prepared by first reacting iridium trichloride hydrate with the 2-phenylpyridine, phenylpyrimidine or phenylquinoline, and adding NaOB.

**[0024]** One particularly useful iridium dimer is the hydroxo iridium dimer, having structure VIII below:



**[0025]** This intermediate can be used to prepare compound 1-p by the addition of ethyl acetoacetate.

#### Electronic Device

**[0026]** The present invention also relates to an electronic device comprising at least one photoactive layer positioned between two electrical contact layers, wherein the at least one layer of the device includes the iridium complex of the invention. Devices frequently have additional hole transport and electron transport layers. A typical structure is shown in Figure 1. The device 100 has an anode layer 110 and a cathode layer 150. Adjacent to the anode is a layer 120 comprising hole transport material. Adjacent to the cathode is a layer 140 comprising an electron transport material. Between the hole transport layer and the electron transport layer is the photoactive layer 130.

**[0027]** Depending upon the application of the device 100, the photoactive layer 130 can be a light-emitting layer that is activated by an applied voltage (such as in a light-emitting diode or light-emitting electrochemical cell), a layer of material that responds to radiant energy and generates a signal with or without an applied bias voltage (such as in a photodetector). Examples of photodetectors include photoconductive cells, photoresistors, photoswitches, phototransistors, and phototubes, and photovoltaic cells, as these terms are describe in Markus, John, Electronics and Nucleonics Dictionary, 470 and 476 (McGraw-Hill, Inc. 1966).

**[0028]** The iridium compounds of the invention are particularly useful as the photoactive material in layer 130, or as electron transport material in layer 140. Preferably the iridium complexes of the invention are used as the light-emitting material in diodes. It has been found that in these applications, the fluorinated compounds of the invention do not need to be in a solid matrix diluent in order to be effective. A layer that is greater than 20% by weight iridium compound, based on the total weight of the layer, up to 100% iridium compound, can be used as the emitting layer. This is in contrast to the non-fluorinated iridium compound, tris(2-phenylpyridine) iridium (III), which was found to achieve maximum efficiency when present in an amount of only 6-8% by weight in the emitting layer. This was necessary to reduce the self-quenching

effect. Additional materials can be present in the emitting layer with the iridium compound. For example, a fluorescent dye may be present to alter the color of emission. A diluent may also be added. The diluent can be a polymeric material, such as poly(N-vinyl carbazole) and polysilane. It can also be a small molecule, such as 4,4'-N,N'-dicarbazole biphenyl or tertiary aromatic amines. When a diluent is used, the iridium compound is generally present in a small amount, usually less than 20% by weight, preferably less than 10% by weight, based on the total weight of the layer.

**[0029]** In some cases the iridium complexes may be present in more than one isomeric form, or mixtures of different complexes may be present. It will be understood that in the above discussion of OLEDs, the term "the iridium compound" is intended to encompass mixtures of compounds and/or isomers.

**[0030]** To achieve a high efficiency LED, the HOMO (highest occupied molecular orbital) of the hole transport material should align with the work function of the anode, the LUMO (lowest un-occupied molecular orbital) of the electron transport material should align with the work function of the cathode. Chemical compatibility and sublimation temp of the materials are also important considerations in selecting the electron and hole transport materials.

**[0031]** The other layers in the OLED can be made of any materials which are known to be useful in such layers. The anode 110, is an electrode that is particularly efficient for injecting positive charge carriers. It can be made of, for example materials containing a metal, mixed metal, alloy, metal oxide or mixed-metal oxide, or it can be a conducting polymer. Suitable metals include the Group 11 metals, the metals in Groups 4, 5, and 6, and the Group 8-10 transition metals. If the anode is to be light-transmitting, mixed-metal oxides of Groups 12, 13 and 14 metals, such as indium-tin-oxide, are generally used. The IUPAC numbering system is used throughout, where the groups from the Periodic Table are numbered from left to right as 1-18 (CRC Handbook of Chemistry and Physics, 81st Edition, 2000). The anode 110 may also comprise an organic material such as polyaniline as described in "Flexible light-emitting diodes made from soluble conducting polymer," Nature vol. 357, pp 477-479 (11 June 1992). At least one of the anode and cathode should be at least partially transparent to allow the generated light to be observed.

**[0032]** Examples of hole transport materials for layer 120 have been summarized for example, in Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Vol. 18, p. 837-860, 1996, by Y. Wang. Both hole transporting molecules and polymers can be used. Commonly used hole transporting molecules are: N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino) phenyl]cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamine (ETPD), tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine (PDA), a-phenyl-4-N,N-diphenylaminostyrene (TPS), p-(diethylamino)-benzaldehyde diphenylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), 1-phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl] pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB), N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB), and porphyrinic compounds, such as copper phthalocyanine. Commonly used hole transporting polymers are polyvinylcarbazole, (phenylmethyl)polysilane, and polyaniline. It is also possible to obtain hole transporting polymers by doping hole transporting molecules such as those mentioned above into polymers such as polystyrene and polycarbonate.

**[0033]** Examples of electron transport materials for layer 140 include metal chelated oxinoid compounds, such as tris (8-hydroxyquinolato)aluminum (Alq<sub>3</sub>); phenanthroline-based compounds, such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DDPA) or 4,7-diphenyl-1,10-phenanthroline (DPA), and azole compounds such as 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD) and 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole (TAZ). Layer 140 can function both to facilitate electron transport, and also serve as a buffer layer or confinement layer to prevent quenching of the exciton at layer interfaces. Preferably, this layer promotes electron mobility and reduces exciton quenching.

**[0034]** The cathode 150, is an electrode that is particularly efficient for injecting electrons or negative charge carriers. The cathode can be any metal or nonmetal having a lower work function than the anode. Materials for the cathode can be selected from alkali metals of Group 1 (e.g., Li, Cs), the Group 2 (alkaline earth) metals, the Group 12 metals, including the rare earth elements and lanthanides, and the actinides. Materials such as aluminum, indium, calcium, barium, samarium and magnesium, as well as combinations, can be used. Li-containing organometallic compounds can also be deposited between the organic layer and the cathode layer to lower the operating voltage.

**[0035]** It is known to have other layers in organic electronic devices. For example, there can be a layer (not shown) between the conductive polymer layer 120 and the active layer 130 to facilitate positive charge transport and/or band-gap matching of the layers, or to function as a protective layer. Similarly, there can be additional layers (not shown) between the active layer 130 and the cathode layer 150 to facilitate negative charge transport and/or band-gap matching between the layers, or to function as a protective layer. Layers that are known in the art can be used. In addition, any of the above-described layers can be made of two or more layers. Alternatively, some or all of inorganic anode layer 110, the conductive polymer layer 120, the active layer 130, and cathode layer 150, may be surface treated to increase charge carrier transport efficiency. The choice of materials for each of the component layers is preferably determined by balancing the goals of providing a device with high device efficiency.

**[0036]** It is understood that each functional layer may be made up of more than one layer.

**[0037]** The device can be prepared by sequentially vapor depositing the individual layers on a suitable substrate. Substrates such as glass and polymeric films can be used. Conventional vapor deposition techniques can be used, such

as thermal evaporation, chemical vapor deposition, and the like. Alternatively, the organic layers can be coated from solutions or dispersions in suitable solvents, using any conventional coating technique. In general, the different layers will have the following range of thicknesses: anode 110, 500-5000Å, preferably 1000-200Å; hole transport layer 120, 50-1000Å, preferably 200-800Å; light-emitting layer 130, 10-1000 Å, preferably 100-800Å; electron transport layer 140, 50-1000Å, preferably 200-800Å; cathode 150, 200-10000Å, preferably 300-5000Å. The location of the electron-hole recombination zone in the device, and thus the emission spectrum of the device, can be affected by the relative thickness of each layer. Thus the thickness of the electron-transport layer should be chosen so that the electron-hole recombination zone is in the light-emitting layer. The desired ratio of layer thicknesses will depend on the exact nature of the materials used.

**[0038]** It is understood that the efficiency of devices made with the iridium compounds of the invention, can be further improved by optimizing the other layers in the device. For example, more efficient cathodes such as Ca, Ba or LiF can be used. Shaped substrates and novel hole transport materials that result in a reduction in operating voltage or increase quantum efficiency are also applicable. Additional layers can also be added to tailor the energy levels of the various layers and facilitate electroluminescence.

**[0039]** The iridium complexes of the invention often are phosphorescent and photoluminescent and may be useful in applications other than OLEDs. For example, organometallic complexes of iridium have been used as oxygen sensitive indicators, as phosphorescent indicators in bioassays, and as catalysts. The bis cyclometalated complexes can be used to synthesize tris cyclometalated complexes where the third ligand is the same or different.

## EXAMPLES

**[0040]** The following examples illustrate certain features and advantages of the present invention. They are intended to be illustrative of the invention, but not limiting. All percentages are by weight, unless otherwise indicated.

### EXAMPLE 1

**[0041]** This example illustrates the preparation of the 2-phenylpyridines and 2-phenylpyrimidines which are used to form the iridium compounds.

**[0042]** The general procedure used was described in O. Lohse, P. Thevenin, E. Waldvogel Synlett, 1999, 45-48. In a typical experiment, a mixture of 200 ml of degassed water, 20 g of potassium carbonate, 150 ml of 1,2-dimethoxyethane, 0.5 g of Pd(PPh<sub>3</sub>)<sub>4</sub>, 0.05 mol of a substituted 2-chloropyridine (quinoline or pyrimidine) and 0.05 mol of a substituted phenylboronic acid was refluxed (80-90°C) for 16-30 h. The resulting reaction mixture was diluted with 300 ml of water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 100 ml). The combined organic layers were dried over MgSO<sub>4</sub>, and the solvent removed by vacuum. The liquid products were purified by fractional vacuum distillation. The solid materials were recrystallized from hexane. The typical purity of isolated materials was >98%. The starting materials, yields, melting and boiling points of the new materials are given in Table 3. NMR data and analytical data are given in Table 4.

**TABLE 3**  
**Preparation of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines**

Compound	Yield in %	B.p./ mm Hg (m.p.) in °C
2-s	70	---
2-a	72	---
2-b	48	---
2-u	75	(76-78)
2-c	41	(95-96)
2-d	38	(39-40)
2-e	55	74.5/0.1
2-g	86	71-73/0.07
2-t	65	77-78/0.046
2-k	50	(38-40)
2-m	80	72-73/0.01
2-f	22	52-33/0.12
2-v	63	95-96/13
2-w	72	
2-x	35	61-62/0.095

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(continued)

Preparation of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines

Compound	Yield in %	B.p./ mm Hg (m.p.) in °C
2-y	62	(68-70)
2-z	42	66-67/0.06 (58-60)
2-aa	60	

TABLE 4

Properties of 2-Phenyl Pyridines, Phenylpyrimidines and Phenylquinolines

Compound	<sup>1</sup> H NMR	<sup>19</sup> F NMR	Analysis %, found (calc.) or MS (M <sup>+</sup> )
2-s	7.48(3H), 7.70(1H), 7.83(1H), 7.90(2H), 8.75(1H)	-62.68	C, 64.50 (64.57) H, 3.49 (3.59) N, 6.07 (6.28)
2-a	7.19(1H), 7.30(1H), 7.43(1H), 7.98(2H), 8.07 (1H) 9.00(1H)	-60.82 (3F, s), -116.96 (1F, m)	C, 59.56 (59.75) H, 3.19 (2.90) N, 5.52 (5.81)
2-b	7.58(1H), 7.66(1H), 7.88(1H), 8.03(1H), 8.23(1H), 8.35 (1H) 8.99(1H)	-62.75 (3F, s), -63.10 (3F, s)	C, 53.68 (53.60) H, 2.61 (2.40) N, 4.53 (4.81)
2-u	7.55(1H), 7.63(1H), 7.75(2H), 7.89(2H), 8.28(2H), 8.38(1H), 8.50 (1H)	-62.89 (s)	C, 69.17 (70.33) H, 3.79 (3.66) N, 4.88 (5.12)
2-c	7.53(1H), 7.64(1H), 7.90(1H), 8.18(1H), 8.30(1H), 8.53(1H), 9.43(1H)	-62.14 (s)	C, 53.83 (53.73) H, 2.89 (2.61) N, 9.99 (10.44)
2-d	7.06(1H), 7.48(1H), 7.81(3H), 8.01(1H), 8.95(1H),	-62.78 (3F, s), -112.61 (1F, m)	C, 59.73 (59.75) H, 2.86 (2.90) N, 5.70 (5.81)
2-e	3.80(3H) 6.93(2H), 7.68(1H), 7.85(1H), 7.96(2H), 8.82(1H),	-62.63 (s)	C, 61.66 (61.90) H, 3.95 (4.04) N, 5.53 (5.38)
2-g	2.70(3H) 7.10(3H), 7.48(1H), 7.60(1H), 8.05(2H),	-114.03 (m)	C, 76.56 (77.00) H, 5.12 (5.30) N, 5.43 (7.50)
2-t	7.10(2H), 7.35(2H), 7.96(1H), 8.78(1H),	-62.73 (3F, s) -113.67 (1F, m)	C, 50.51 (52.17) H, 1.97 (2.17) N, 5.09 (5.07)
2-k	7.08(2H), 7.62(1H), 7.90(3H), 8.80(1H),	-62.75 (3F, s) -111.49 (m)	C, 60.39 (59.75), H, 3.38 (2.90), N, 5.53 (5.51)
2-m	7.10(2H), 7.80(2H), 8.00(1H), 8.75(1H),	-62.63 (3F, s) -111.24 (m)	C, 52.13 (52.17) H, 2.16 (2.17) N, 4.85 (5.07)
2-f	7.55(3H), 7.77(2H), 8.06(1H), 8.87(1H)	-62.57(s)	257(M <sup>+</sup> , C <sub>12</sub> H <sub>7</sub> F <sub>3</sub> ClN <sup>+</sup> ), 222 (M-Cl)
2-v	3.8(3H), 6.95(1H), 7.30(1H), 7.50(1H), 7.58(1H), 7.75(1H), 7.90(1H), 8.87(1H)	-62.70 ppm	C, 61.66 (61.37), H, 3.98 (3.67), N, 5.53 (5.48)

(continued)

	Compound	<sup>1</sup> H NMR	<sup>19</sup> F NMR	Analysis %, found (calc.) or MS (M <sup>+</sup> )
5	2-w	8.54 (1H, d), 8.21 (2H, d), 7.70 (2H, d), 7.24 (1H, s), 6.82 (1H, dd), 3.91 (3H, s)	-63.08 (3F, s)	
	2-x	6.9 (2H, m), 7.18 (2H, m), 7.68 (2H, m), 7.95 (1H, m), 8.65 (1H, m);	-109.70 (1F, m), -113.35 (1F, m).	
10	2-y	6.94 (1H), 7.62 (2H), 7.82 (1H), 8.03 (1H), 8.96 (1H);	-62.72 (3F, s), -109.11 (2F, m)	
	2-z	6.85 (1H), 6.93 (1H), 7.80, 7.90, 8.05 (3H), 8.89 (1H);	-62.80 (3F, s), -107.65 (1F, m), -112.45 (1F, m).	
15	2-aa	7.70 (3H, m), 7.85 (3H, m), 7.80, 7.90, 8.85 (1H, m).		

**EXAMPLE 2**

20 **[0043]** This example illustrates the preparation of iridium complexes of the Formula  $\text{IrL}^{\text{a}}\text{L}^{\text{b}}\text{L}^{\text{c}}\text{L}^{\text{d}}$  above.

**Compound 1-n**

25 **[0044]** A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 510 mg), 2-(3-trifluoromethylphenyl)-quinoline (1.80 g), and silver trifluoroacetate (1.10 g) was vigorously stirred at 190-195°C for 4 hours. The resulting solid was chromatographed on silica with dichloromethane to produce a mixture of the dicyclopentadienyl complex and the unreacted ligand. The latter was removed from the mixture by extraction with warm hexanes. After the extracts became colorless the hexane-insoluble solid was collected and dried under vacuum. The yield was 0.29 g. <sup>19</sup>F NMR: -63.5 (s, 6F), -76.5 (s, 3F). The structure of this complex was established by a single crystal X ray diffraction study.

**Compound 1-o**

35 **[0045]** A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 500 mg), 2-(2-fluorophenyl)-3-chloro-5-trifluoromethylpyridine (2.22 g), water (0.3 mL), and silver trifluoroacetate (1.00 g) was stirred at 190°C for 1.5 hours. The solid product was chromatographed on silica with dichloromethane to produce 0.33 g of a 2:1 co-crystallized adduct of the dicyclopentadienyl aqua trifluoroacetato complex, compound 1-p, and the unreacted ligand. <sup>19</sup>F NMR: -63.0 (9F), -76.5 (3F), -87.7 (2F), -114.4 (1F). The co-crystallized phenylpyridine ligand was removed by recrystallization from dichloromethane-hexanes. The structures of both the adduct and the complex were established by a single crystal X-ray diffraction study.

**EXAMPLE 3**

40 **[0046]** This example illustrates the preparation of an hydroxo iridium dimer, having structure (VIII) above.

45 **[0047]** A mixture of  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (54% Ir; 510 mg), 2-(4-fluorophenyl)-5-trifluoromethylpyridine (725 mg), water (5 mL), and 2-ethoxyethanol (20 mL) was vigorously stirred under reflux for 4.5 hours. After a solution of NaOH (2.3 g) in water (5 mL) was added, followed by 20 mL of water, the mixture was stirred under reflux for 2 hours. The mixture was cooled down to room temperature, diluted with 50 mL of water, and filtered. The solid was vigorously stirred under reflux with 30 mL of 1,2-dichloroethane and aqueous NaOH (2.2 g in 8 mL of water) for 6 hours. The organic solvent was evaporated from the mixture to leave a suspension of an orange solid in the aqueous phase. The orange solid was separated by filtration, thoroughly washed with water, and dried under vacuum to produce 0.94 g (95%) of the iridium hydroxo dimer (spectroscopically pure). <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ ): -1.0 (s, 1H, IrOH), 5.5 (dd, 2H), 6.6 (dt, 2H), 7.7 (dd, 2H), 7.9 (dd, 2H), 8.0 (d, 2H), 9.1 (d, 2H). <sup>19</sup>F NMR ( $\text{CD}_2\text{Cl}_2$ ): -62.5 (s, 3F), -109.0 (ddd, 1F).

**EXAMPLE 4**

55 **[0048]** This example illustrates the preparation of bis-cyclopentadienyl complexes from an iridium dimer.

Compounds 1-p

**[0049]** A mixture of the iridium hydroxo dimer (100 mg) from Example 4, ethyl acetoacetate (0.075 mL; 4-fold excess), and dichloromethane (4 mL) was stirred at room temperature overnight. The solution was filtered through a short silica plug and evaporated to give an orange-yellow solid which was washed with hexanes and dried. The yield of the complex was 109 mg (94%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.1 (t, CH<sub>3</sub>), 3.9 (dm, CH<sub>2</sub>), 4.8 (s, CH<sub>3</sub>COCH), 5.9 (m), 6.7 (m), 7.7 (m), 8.0 (m), 8.8 (d). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>): -63.1 (s, 3F), -63.2 (s, 3F), -109.1 (ddd, 1F), -109.5 (ddd). Analysis: Calcd: C, 44.9; H, 2.6; N, 3.5. Found: C, 44.4; H, 2.6; N, 3.3.

Compound 1-w

**[0050]** A solution of hydroxo iridium dimer from Example 4 (0.20 g) in THF (6 mL) was treated with 50 mg of trifluoroacetic acid, filtered through a short silica plug, evaporated to ca. 0.5 mL, treated with hexanes (8 mL), and left overnight. The yellow crystalline solid was separated, washed with hexanes, and dried under vacuum. Yield (1:1 THF solvate): 0.24 g (96%). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), δ: -63.2 (s, 3F), -76.4 (s, 3F), -107.3 (ddd, 1F). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), δ: 9.2 (br s, 1H), 8.2 (dd, 1H), 8.1 (d, 1H), 7.7 (m, 1H), 6.7 (m, 1H), 5.8 (dd, 1H), 3.7 (m, 2H, THF), 1.8 (m, 2H, THF).

Compound 1-x

**[0051]** A mixture of the trifluoroacetate intermediate, compound 1-w (75 mg), and 2-(4-bromophenyl)-5-bromopyridine (130 mg) was stirred under N<sub>2</sub> at 150-155 °C for 30 min. The resulting solid was cooled to room temperature and dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was filtered through silica gel and evaporated. The residue was washed several times with warm hexanes and dried under vacuum to leave a yellow, yellow-photoluminescent solid. Yield: 74 mg (86%). <sup>19</sup>F NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), δ: -63.1 (s, 3F), -63.3 (s, 3F), -108.8 (ddd, 1F), -109.1 (ddd, 1F). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C), δ: 8.2 (s), 7.9 (m), 7.7 (m), 7.0 (d), 6.7 (m), 6.2 (dd), 6.0 (dd). The complex was meridional, with the nitrogens of the fluorinated ligands being trans, as confirmed by X-ray analysis.

EXAMPLE 5

**[0052]** This example illustrates the formation of OLEDs using the iridium complexes of the invention.

**[0053]** Thin film OLED devices including a hole transport layer (HT layer), electroluminescent layer (EL layer) and at least one electron transport layer (ET layer) were fabricated by the thermal evaporation technique. An Edward Auto 306 evaporator with oil diffusion pump was used. The base vacuum for all of the thin film deposition was in the range of 10<sup>-6</sup> torr. The deposition chamber was capable of depositing five different films without the need to break up the vacuum.

**[0054]** An indium tin oxide (ITO) coated glass substrate was used, having an ITO layer of about 1000-2000 Å. The substrate was first patterned by etching away the unwanted ITO area with IN HCl solution, to form a first electrode pattern. Polyimide tape was used as the mask. The patterned ITO substrates were then cleaned ultrasonically in aqueous detergent solution. The substrates were then rinsed with distilled water, followed by isopropanol, and then degreased in toluene vapor for ~3 hours.

**[0055]** The cleaned, patterned ITO substrate was then loaded into the vacuum chamber and the chamber was pumped down to 10<sup>-6</sup> torr. The substrate was then further cleaned using an oxygen plasma for about 5-10 minutes. After cleaning, multiple layers of thin films were then deposited sequentially onto the substrate by thermal evaporation. Finally, patterned metal electrodes of A1 were deposited through a mask. The thickness of the film was measured during deposition using a quartz crystal monitor (Sycon STC-200). All film thickness reported in the Examples are nominal, calculated assuming the density of the material deposited to be one. The completed OLED device was then taken out of the vacuum chamber and characterized immediately without encapsulation.

**[0056]** A summary of the device layers and thicknesses is given in Table 6. In all cases the anode was ITO as discussed above, and the cathode was A1 having a thickness in the range of 700-760 Å. In some of the samples, a two-layer electron transport layer was used. The layer indicated first was applied adjacent to the EL layer.

TABLE 6

Alq<sub>3</sub> = tris(8-hydroxyquinololato) aluminum  
 DDPA = 2,9-dimethyl-4,7,7-diphenyl-1,10-phenanthroline  
 Ir(ppy)<sub>3</sub> = fac-tris(2-phenylpyridine) iridium  
 MPMP = bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane

Sample	HT layer (Thickness, Å)	EL layer (Thickness, Å)	ET layer (Thickness, Å)
Comparative	MPMP (528)	Ir(ppy) <sub>3</sub> (408)	DDPA (106) + Alq <sub>3</sub> (320)
1	MPMP (520)	Compound 1-n (419)	DDPA (420)
2	MPMP (511)	Compound 1-o (412)	DDPA (413)
3	MPMP (527)	Compound 1-p (425)	DDPA (412)

**[0057]** The OLED samples were characterized by measuring their (1) current-voltage (I-V) curves, (2) electroluminescence radiance versus voltage, and (3) electroluminescence spectra versus voltage. The apparatus used, 200, is shown in Figure 2. The I-V curves of an OLED sample, 220, were measured with a Keithley Source-Measurement Unit Model 237, 280. The electroluminescence radiance (in the unit of Cd/m<sup>2</sup>) vs. voltage was measured with a Minolta LS-110 luminescence meter, 210, while the voltage was scanned using the Keithley SMU. The electroluminescence spectrum was obtained by collecting light using a pair of lenses, 230, through an electronic shutter, 240, dispersed through a spectrograph, 250, and then measured with a diode array detector, 260. All three measurements were performed at the same time and controlled by a computer, 270. The efficiency of the device at certain voltage is determined by dividing the electroluminescence radiance of the LED by the current density needed to run the device. The unit is in Cd/A.

**[0058]** The results are given in Table 7 below:

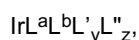
TABLE 7  
 Electroluminescent Properties of Iridium Compounds

Sample	Peak Radiance, Cd/m <sup>2</sup>	Efficiency at peak radiance, Cd/A	Peak efficiency, Cd/A	Approximate Peak Wavelengths, nm
Comparative	540 at 22 V	0.39	0.48	522
1	3.5 at 28 V	0.005	0.014	575
2	30 at 26 V	0.08	0.16	590
3	2000 at 21 V	6	8	532

**[0059]** The peak efficiency is the best indication of the value of the electroluminescent compound in a device. It gives a measure of how many electrons have to be input into a device in order to get a certain number of photons out (radiance). It is a fundamentally important number, which reflects the intrinsic efficiency of the light-emitting material. It is also important for practical applications, since higher efficiency means that fewer electrons are needed in order to achieve the same radiance, which in turn means lower power consumption. Higher efficiency devices also tend to have longer lifetimes, since a higher proportion of injected electrons are converted to photons, instead of generating heat or causing an undesirable chemical side reactions. Most of the iridium complexes of the invention have much higher peak efficiencies than the parent fac-tris(2-phenylpyridine) iridium complex. Those complexes with lower efficiencies may also find utility as phosphorescent or photoluminescent materials, or as catalysts, as discussed above.

## Claims

1. An organic electronic device comprising an emitting layer comprising at least one iridium compound having a formula below:



where:

$y=0, 1$  or  $2$ , and  $z=0$  or  $1$ , with the proviso that:

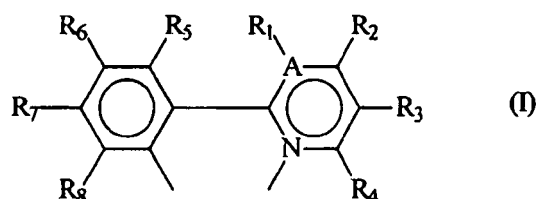
when  $y=2$  then  $z=0$ ;

$L'$  = a bidentate ligand or a monodentate ligand, and is not a phenylpyridine, phenylpyrimidine, or phenylquinoline; with the proviso that:

when  $L'$  is a monodentate ligand,  $y+z=2$ , and

when  $L'$  is a bidentate ligand,  $z=0$ ;

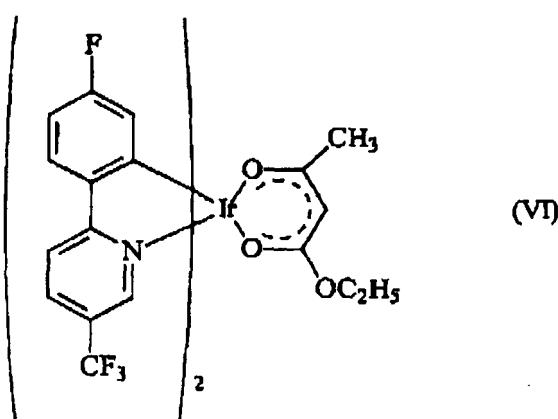
$L''$  = a monodentate ligand, and is not a phenylpyridine, and phenylpyrimidine, or phenylquinoline; and  $L^a$  and  $L^b$  are alike or different from each other and each of  $L^a$  and  $L^b$  has structure (I) below:



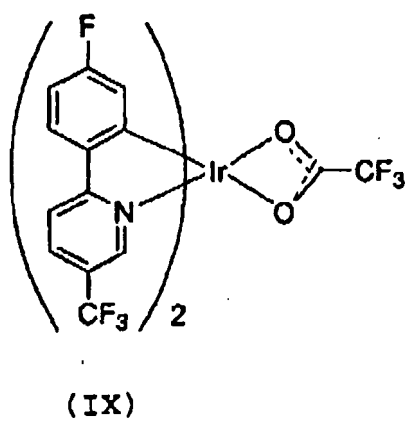
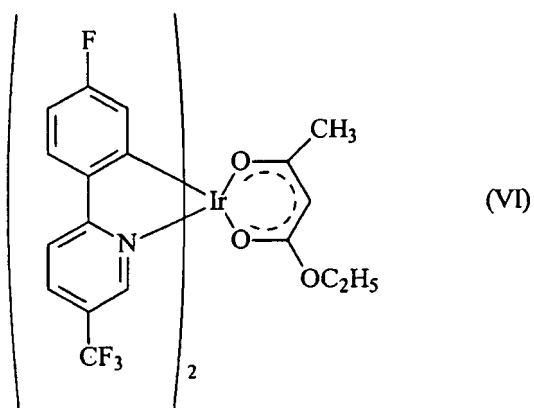
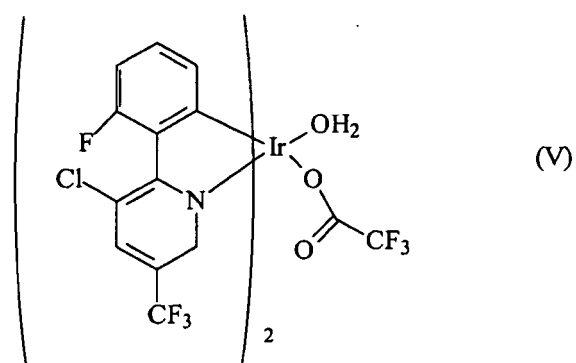
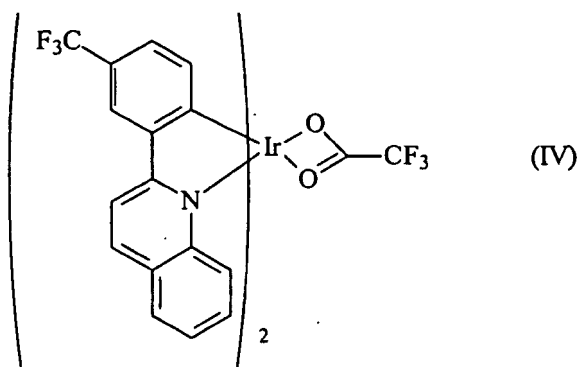
wherein:

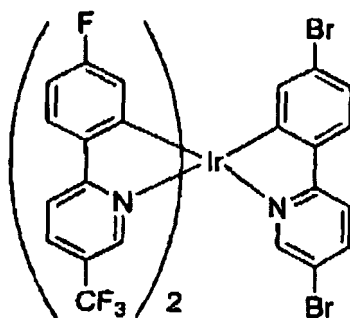
adjacent pairs of  $R_1$ - $R_4$  and  $R_5$ - $R_8$  can be joined to form a five- or six-membered ring, at least one of  $R_1$ - $R_8$  is selected from F,  $C_nF_{2n+1}$ ,  $OC_nF_{2n+1}$ , and  $OCF_2X$ , where  $n=1-6$  and  $X=H, Cl, \text{ or } Br$ , and  $A=C$  or  $N$ , provided that when  $A=N$ , there is no  $R_1$ , and with the proviso that when the iridium compound is present in an amount of less than 20% by weight of the emitting layer, the emitting layer comprises a diluent.

2. The device of claim 1 wherein the iridium compound is present in an amount of at least 20% by weight of the emitting layer.
3. The device of claim 2 wherein  $R_3$  is  $CF_3$ .
4. The device of claim 3 wherein at least one of  $R_3$ - $R_8$  is selected from F,  $C_nF_{2n+1}$ ,  $OC_nF_{2n+1}$  and  $OCF_2X$ , where  $n = 1-6$  and  $x = H, Cl, \text{ or } Br$ .
5. The device of claim 2 wherein  $y = 1$ , the iridium compound having a structure (VI) below:



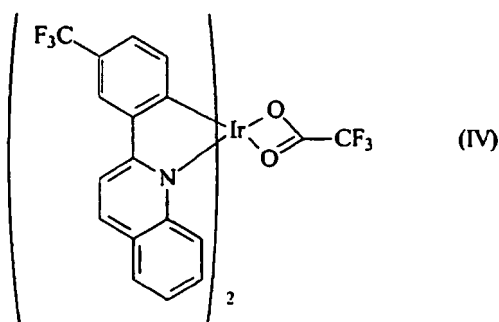
6. An organic electronic device as claimed in claim 1 comprising an emitting layer that comprises a compound having one of the structures (IV), (V), (VI), (IX) and (X) below:



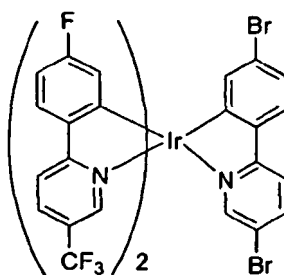
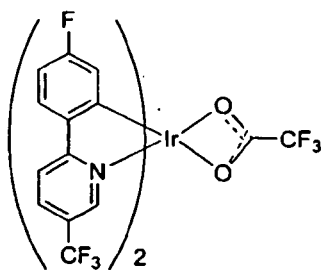
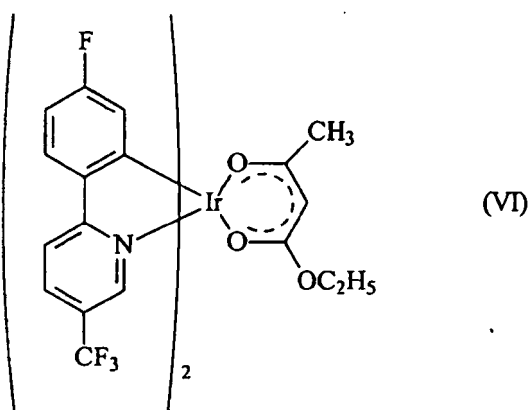
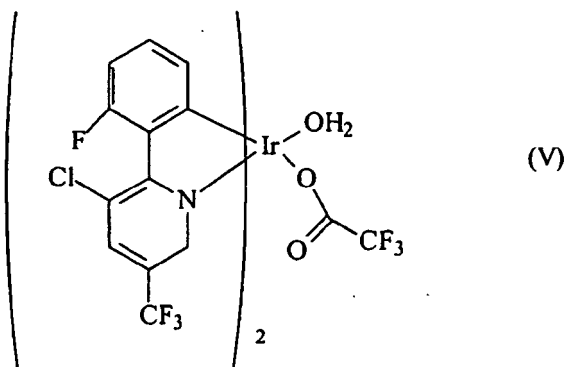


(X)

7. The device of claim 6 wherein the emitting layer further comprises a diluent.
8. The device of claim 1 or claim 7 wherein the diluent is selected from poly(N-vinyl carbazole), polysilane, 4,4'-N,N'-dicarbazole biphenyl, and tertiary aromatic amines.
9. The device of any one of claims 1 to 8, further comprising a hole transport layer selected from N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD), 1,1-bis[(di-4-tolylamino)phenyl]-cyclohexane (TAPC), N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamine (ETPD), tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylenediamine (PDA),  $\alpha$ -phenyl-4-N,N-diphenylaminostyrene (TPS), p-(diethylamino)-benzaldehyde diphenylhydrazone (DEH), triphenylamine (TPA), bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), 1-phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl] pyrazoline (PPR or DEASP), 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB), N,N,N',N'-tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TTB), porphyrinic compounds, and combinations thereof.
10. The device of any one of claims 1 to 9 further comprising an electron transport layer selected from tris(8-hydroxyquinolato)aluminium, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (DDPA), 4,7-diphenyl-1,10-phenanthroline (DPA), 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole (PBD), 3-(4-biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazole (TAZ), and combinations thereof.
11. A compound having a structure selected from structures (IV), (V), (VI), (IX) and (X) below:

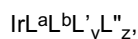


(IV)



## Patentansprüche

1. Organische elektronische Vorrichtung, umfassend eine emittierende Schicht, umfassend mindestens eine Iridium-  
verbindung mit einer nachstehenden Formel:



WO:

y = 0, 1 oder 2, und z = 0 oder 1, mit der Maßgabe, dass:

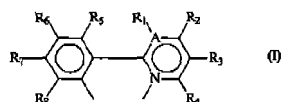
wenn y = 2, dann z = 0;

L' = ein zweizähniger Ligand oder ein einzähniger Ligand, und nicht ein Phenylpyridin, Phenylpyrimidin oder Phenylchinolin, ist; mit der Maßgabe, dass:

wenn L' ein einzähniger Ligand ist, y + z = 2, und

wenn L' ein zweizähniger Ligand ist, z = 0;

L'' = ein einzähniger Ligand, und nicht ein Phenylpyridin und Phenylpyrimidin oder Phenylchinolin, ist; und  
L<sup>a</sup> und L<sup>b</sup> gleich oder voneinander verschieden sind und jedes von L<sup>a</sup> und L<sup>b</sup> nachstehende Struktur (I) hat:



wobei:

benachbarte Paare von R<sub>1</sub>-R<sub>4</sub> und R<sub>5</sub>-R<sub>8</sub> verbunden sein können, um einen fünf- oder sechsgliedrigen Ring zu erzeugen,  
mindestens eines von R<sub>1</sub>-R<sub>8</sub> aus F, C<sub>n</sub>F<sub>2n+1</sub>, OC<sub>n</sub>F<sub>2n+1</sub> und OCF<sub>2</sub>X, WO n = 1-6 und X = H, Cl oder Br, ausgewählt ist, und

A = C oder N, mit der Maßgabe, dass, wenn A = N, es kein R<sub>1</sub> gibt,

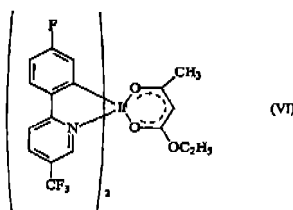
und mit der Maßgabe, dass, wenn die Iridiumverbindung in einem Anteil von weniger als 20 Gew.-% der emittierenden Schicht vorhanden ist, die emittierende Schicht ein Verdünnungsmittel umfasst.

2. Vorrichtung nach Anspruch 1, wobei die Iridiumverbindung in einem Anteil von mindestens 20 Gew.-% der emittierenden Schicht vorhanden ist.

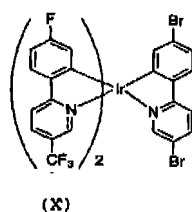
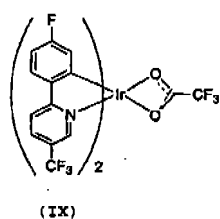
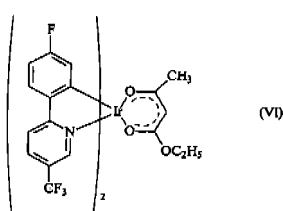
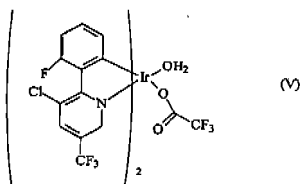
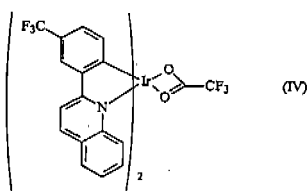
3. Vorrichtung nach Anspruch 2, wobei R<sub>3</sub> CF<sub>3</sub> ist.

4. Vorrichtung nach Anspruch 3, wobei mindestens eines von R<sub>5</sub>-R<sub>8</sub> aus F, C<sub>n</sub>F<sub>2n+1</sub>, OC<sub>n</sub>F<sub>2n+1</sub> und OCF<sub>2</sub>X, WO n = 1-6 und X = H, Cl oder Br, ausgewählt ist.

5. Vorrichtung nach Anspruch 2, wobei y = 1, wobei die Iridiumverbindung eine nachstehende Struktur (VI) hat:



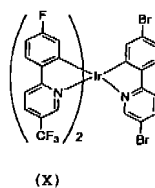
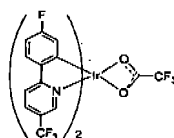
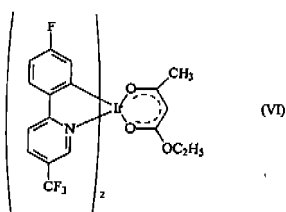
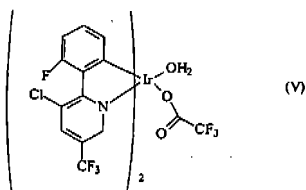
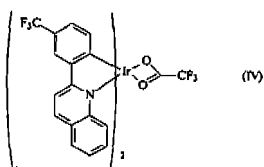
6. Organische elektronische Vorrichtung, wie in Anspruch 1 beansprucht, umfassend eine emittierende Schicht, die eine Verbindung mit einer der nachstehenden Strukturen (IV), (V), (VI), (IX) und (X) umfasst:



7. Vorrichtung nach Anspruch 6, wobei die emittierende Schicht weiterhin ein Verdünnungsmittel umfasst.
8. Vorrichtung nach Anspruch 1 oder Anspruch 7, wobei das Verdünnungsmittel aus Poly(N-vinylcarbazol), Polysilan, 4,4'-N,N'-Dicarbazolbiphenyl und tertiären aromatischen Aminen ausgewählt ist.
9. Vorrichtung nach einem der Ansprüche 1 bis 8, weiterhin umfassend eine Lochtransportschicht, ausgewählt aus N, N'-Diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamin (TPD), 1,1-Bis[(di-4-tolylamino)phenyl]-cyclohexan (TAPC), N,N'-Bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-[1,1'-(3,3'-dimethyl)biphenyl]-4,4'-diamin (ETPD), Tetrakis-(3-methylphenyl)-N,N,N',N'-2,5-phenylendiamin (PDA),  $\alpha$ -Phenyl-4-N,N-diphenylaminostyrol (TPS), p-(Diethylamino)-benzaldehyd-diphenylhydrazon (DEH), Triphenylamin (TPA), Bis[4-(N,N-diethylamino)-2-methylphenyl](4-methylphenyl)methan (MPMP), 1-Phenyl-3-[p-(diethylamino)styryl]-5-[p-(diethylamino)phenyl]pyrazolin (PPR oder DEASP), 1,2-trans-Bis(9H-carbazol-9-yl)cyclobutan (DCZB), N,N,N',N'-Tetrakis(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamin (TTB), porphyrinischen Verbindungen und Kombinationen davon.
10. Vorrichtung nach einem der Ansprüche 1 bis 9, weiterhin umfassend eine Elektronentransportschicht, ausgewählt

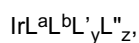
aus Tris(8-hydroxyquinolato)aluminium, 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthrolin (DDPA), 4,7-Diphenyl-1,10-phenanthrolin (DPA), 2-(4-Biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazol (PBD), 3-(4-Biphenyl)-4-phenyl-5-(4-t-butylphenyl)-1,2,4-triazol (TAZ) und Kombinationen davon.

11. Verbindung mit einer Struktur, ausgewählt aus den nachstehenden Strukturen (IV), (V), (VI), (IX) und (X):



## Revendications

1. Dispositif électronique organique comprenant une couche émettrice comprenant au moins un composé d'iridium répondant à la formule ci-dessous:



où:

y=0, 1 ou 2, et z=0 ou 1, sous réserve que:

lorsque  $y=2$  alors  $z=0$ ;

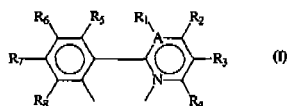
$L'$  = un ligand bidenté ou un ligand monodenté, et n'est pas une phénylpyridine, une phénylpyrimidine, ou une phénylquinoléine; sous réserve que:

lorsque  $L'$  est un ligand monodenté,  $y+z=2$ , et

lorsque  $L'$  est un ligand bidenté,  $z=0$ ;

$L''$  = un ligand monodenté, et n'est pas une phénylpyridine, et une phénylpyrimidine, ou une phénylquinoléine; et

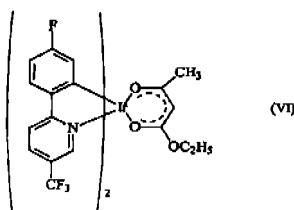
$L^a$  et  $L^b$  sont similaires ou différents et chacun des  $L^a$  et  $L^b$  a une structure (I) ci-dessous:



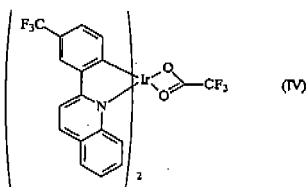
dans laquelle:

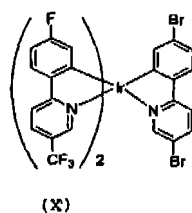
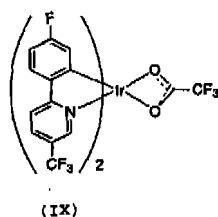
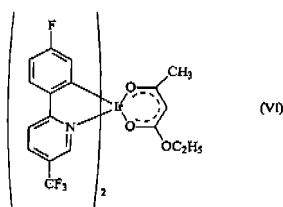
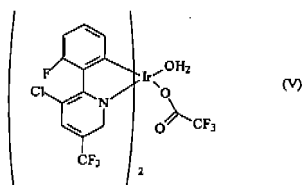
des paires adjacentes de  $R_1$ - $R_4$  et de  $R_5$ - $R_8$  peuvent être réunies pour former un cycle à cinq ou six chaînons, au moins un des  $R_1$ - $R_8$  est choisi parmi F,  $C_nF_{2n+1}$ ,  $OC_nF_{2n+1}$ , et  $OCF_2X$ , où  $n=1-6$  et  $X=H$ , Cl, ou Br, et  $A=C$  ou N, sous réserve que lorsque  $A=N$ , il n'y a pas de  $R_1$ , et sous réserve que lorsque le composé d'iridium est présent en une quantité inférieure à 20% en poids de la couche émettrice, la couche émettrice comprend un diluant.

2. Dispositif selon la revendication 1 dans lequel le composé d'iridium est présent en une quantité d'au moins 20% en poids de la couche émettrice.
3. Dispositif selon la revendication 2 dans lequel  $R_3$  est  $CF_3$ .
4. Dispositif selon la revendication 3 dans lequel au moins un des  $R_5$ - $R_8$  est choisi parmi F,  $C_nF_{2n+1}$ ,  $OC_nF_{2n+1}$  et  $OCF_2X$ , où  $n=1-6$  et  $X=H$ , Cl, ou Br.
5. Dispositif selon la revendication 2 dans lequel  $y=1$ , le composé d'iridium ayant une structure (VI) ci-dessous:

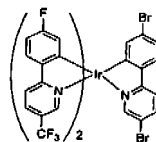
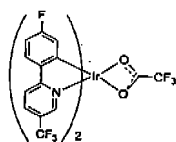
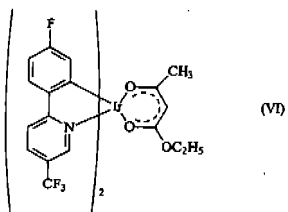
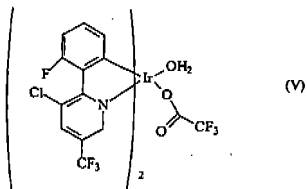
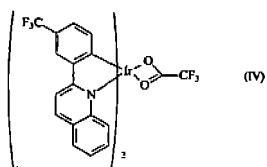


6. Dispositif électronique organique selon la revendication 1 comprenant une couche émettrice qui comprend un composé ayant une des structures (IV), (V), (VI), (IX) et (X) ci-dessous:





7. Dispositif selon la revendication 6 dans lequel la couche émettrice comprend en outre un diluant.
8. Dispositif selon la revendication 1 ou la revendication 7 dans lequel le diluant est choisi parmi le poly(N-vinylcarbazole), le polysilane, le 4,4'-N,N'-dicarbazole biphényle, et les amines aromatiques tertiaires.
9. Dispositif selon l'une quelconque des revendications 1 à 8, comprenant en outre une couche de transport de trous choisie parmi la N,N'-diphényl-N,N'-bis(3-méthylphényl)-[1,1'-biphényl]-4,4'-diamine (TPD), le 1,1-bis[(di-4-tolylamino)phényl]cyclohexane (TAPC), la N,N'-bis(4-méthylphényl)-N,N'-bis(4-éthylphényl)-[1,1'-(3,3'-diméthyl)biphényl]-4,4'-diamine (ETPD), la tétrakis-(3-méthylphényl)-N,N,N',N'-2,5-phénylènediamine (PDA), l' $\alpha$ -phényl-4-N,N-diphénylaminostyrène (TPS), la p-(diéthylamino)benzaldéhyde diphénylhydrazone (DEH), la triphénylamine (TPA), le bis[4-(N,N-diéthylamino)-2-méthylphényl](4-méthylphényl)méthane (MPMP), la 1-phényl-3-[p-(diéthylamino)styril]-5-[p-(diéthylamino)phényl]pyrazoline (PPR ou DEASP), le 1,2-trans-bis(9H-carbazol-9-yl)cyclobutane (DCZB), la N,N,N',N'-tétrakis(4-méthylphényl)-(1,1'-biphényl)-4,4'-diamine (TTB), les composés porphyriniques, et les combinaisons de ceux-ci.
10. Dispositif selon l'une quelconque des revendications 1 à 9 comprenant en outre une couche de transport d'électrons choisie parmi le tris(8-hydroxyquinolato)aluminium, la 2,9-diméthyl-4,7-diphényl-1,10-phénanthroline (DDPA), la 4,7-diphényl-1,10-phénanthroline (DPA), le 2-(4-biphényl)-5-(4-t-butylphényl)-1,3,4-oxadiazole (PBD), le 3-(4-biphényl)-4-phényl-5-(4-t-butylphényl)-1,2,4-triazole (TAZ), et les combinaisons de ceux-ci.
11. Composé ayant une structure choisie parmi les structures (IV), (V), (VI), (IX) et (X) ci-dessous:



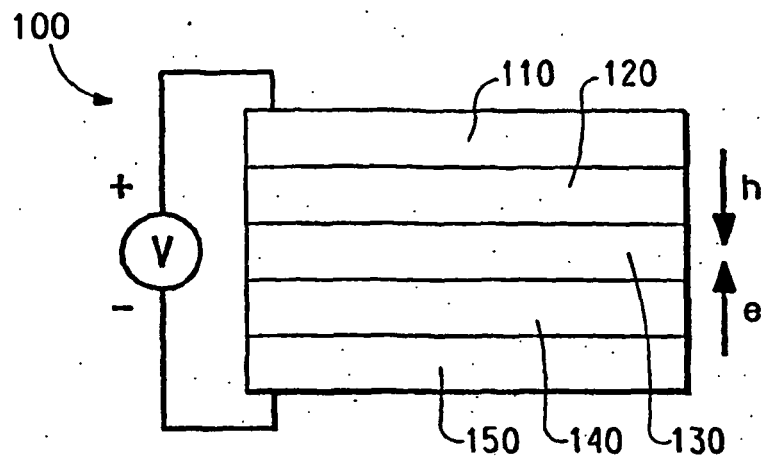


FIG. 1

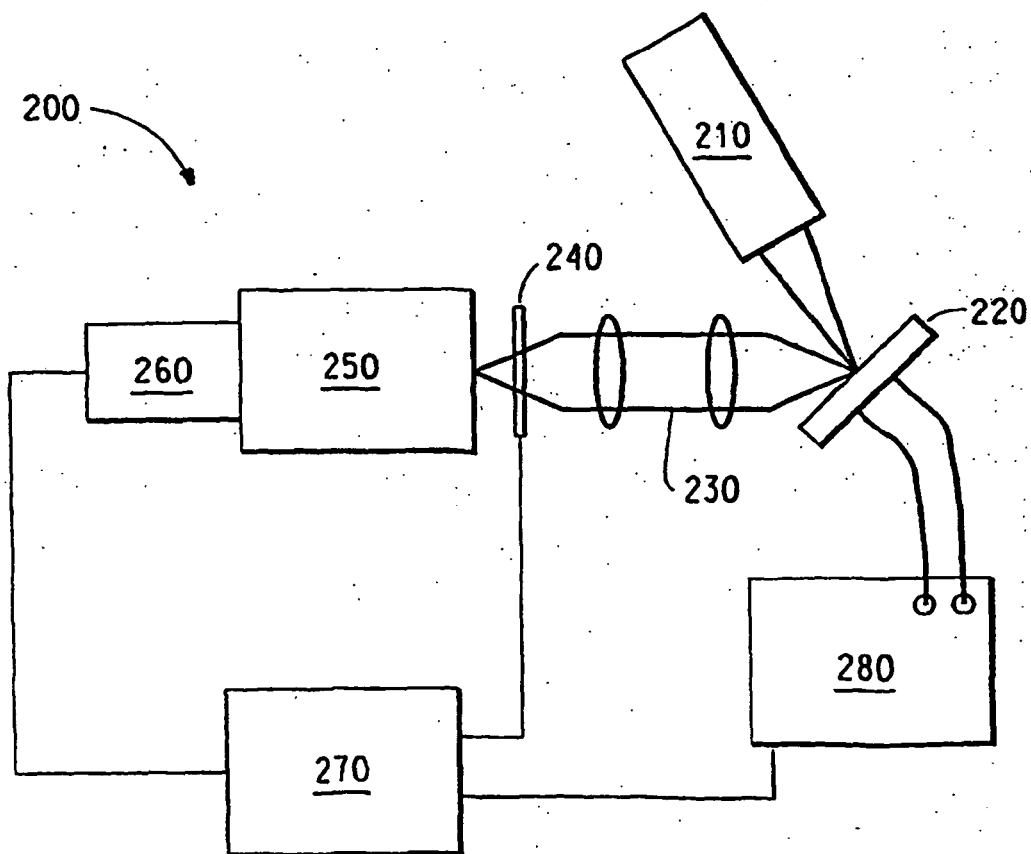


FIG. 2

## REFERENCES CITED IN THE DESCRIPTION

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

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专利名称(译)	具有氟化苯基吡啶，苯基嘧啶和苯基喹啉的电致发光铱化合物和用这些化合物制成的装置		
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#### 摘要(译)

本发明一般涉及电致发光Ir ( III ) 化合物，用于制备Ir ( III ) 化合物的取代的2-苯基吡啶，苯基嘧啶和苯基喹啉，以及用Ir ( III ) 化合物制备的器件。

